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<p>(21) International Application Number: PCT/US92/00985</p> <p>(22) International Filing Date: 5 February 1992 (05.02.92)</p> <p>(30) Priority data: 651,205 6 February 1991 (06.02.91) US</p> <p>(71)(72) Applicant and Inventor: SMITH, Ronald, J. [US/US]; 504 Wittich Terrace, River Vale, NJ 07675 (US).</p> <p>(74) Agent: ZALL, Michael, E.; Weingram &amp; Zall, P.O. Box 927, Maywood, NJ 07607 (US).</p> <p>(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent).</p>		<p>Published <i>With international search report.</i></p>
<p>(54) Title: QUATERNIZED PANTHENOL COMPOUNDS AND THEIR USE</p> <div style="text-align: center; margin-top: 100px;"> <math display="block">  \begin{array}{c}  \oplus R_1 \\  R - N - R_3 - CH - CH_2 \\    \quad   \\  R_2 \quad OH \cdot O - CH_2  \end{array}  \begin{array}{c}  CH_3 \quad OH \\    \quad   \\  C - C - O - NH - CH_2 - CH_2 - CH_2 - OH \cdot X^\ominus \\    \quad   \\  CH_3 \quad H  \end{array}  \quad (I)  </math> </div>		
<p>(57) Abstract</p> <p>Quaternized panthenol compounds of formula (I), wherein R, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each independently, straight or branched chain alkyl of 1 to 24 carbon atoms.</p>		

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Title: QUATERNIZED PANTHENOL COMPOUNDS AND THEIR  
USE

S P E C I F I C A T I O N  
BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

This invention relates to functional ingredients for cosmetic products, in particular quaternized panthenol compounds having enhanced substantivity in cosmetic products.

2. PRIOR ART

Hair and skin conditioners are functional materials, which are used to improve the appearance and manageability of human hair and the appearance of skin. Contained in such products are cationic compounds, e.g. surfactants, polymers. These compounds provide substantivity of the compositions to hair and skin due to the attachment thereto by means of chemical bonds. For example, following treatment with hair rinses and conditioning shampoos containing such cationic compounds

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5 hair is easier to comb when wet without tangling and there is less "fly-away" when it is combed dry. Moreover it is softer, smoother, has more gloss, and appears to have more body. In the case of skin conditioners, which often incorporate cationic resins, rinsing with water does not appreciably remove them from the skin.

0 There are a large number of cationic compounds on the market with applications in personal care products. Panthenol is one of these well known compounds suitable for incorporation into cosmetic formulations. Panthenol is a stable, biologically active form of pantothenic acid. Panthenol has been incorporated into a number of well-known commercial cosmetic and pharmaceutical products with cosmetic and therapeutic effects, for example, creams, hair grooming liquids, lipsticks, 5 aftershave lotions, and aerosol hair sprays, see Rubin, Magid & Scheiner, "Panthenol in Cosmetics", Proc. Sci. Sec. TGA, 32:6 (1959).

10 It is also well-known in the art that cationic quaternary ammonium compounds are effective ingredients in hair conditioning preparations. They are believed to be effective because they possess a positive electrostatic charge, which is attracted by and neutralizes the negative charges of hair protein. The

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mutual attraction of opposite electrostatic charges thus causes the quaternary ammonium compound to remain on the hair. This tendency to remain on the hair is termed substantivity. Substantive quaternary ammonium compounds not only neutralize the electrostatic charges of hair, but can also provide lubricity, by virtue of long chain (fatty) substituents within such compounds.

Other relevant art includes the following US Patents:

10	3,230,228	ERLEMAN ET AL
	3,577,528	MCDONOUGH ET AL
	3,766,267	ZAK ET AL
	4,444,750	GREEN ET AL
	4,631,187	PADDEN ET AL
15	4,764,306	LOGIN
	4,891,214	STEVENS ET AL
	4,923,642	RUTZEN ET AL
	4,940,785	STOBER ET AL
	4,950,468	NAKAMURA ET AL

20 US Patent 3,230,228 to Erlemann et al discloses panthenol ethers and thioethers of a specific formula. Note that at column 1, lines 51-59 the compounds can be converted into an acid addition or quaternary salt if desired.

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US Patent No. 3,577,528 to McDonough et al discloses hair conditioner compositions containing quaternary ammonium compounds containing 15 or more total carbon atoms (column 2, lines 29-38). A preferred quaternary ammonium compound is stearyl dimethyl benzyl ammonium chloride.

US Patent No. 3,766,267 to Zak et al discloses compositions consisting of quaternary halides of trialkyl or hydroxyalkyl amino alkyl gluconamides which show high substantivity for keratinaceous substances. Attention is directed to the formula at the top of column 2, wherein R can be methyl, R' may be C<sub>1</sub> to C<sub>12</sub> alkyl, n is an integer from 2 to 4.

US Patent No. 4,444,750 to Green et al discloses hair conditioners which are linear polymeric quaternary ammonium materials.

US Patent No. 4,631,187 to Padden et al discloses hair care products containing a quaternary compound having one erucic group, i.e. a mixed alkenyl having at least about 65% C<sub>22</sub> olefins derived from erucics, cis-13-docosenoic acid.

US Patent No. 4,764,306 to Logan describes a process for preparing certain bis-quaternary ammonium compounds and mixtures thereof. Note the formula in the middle of columns 3 and 4.

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US Patent No. 4,891,214 to Stevens et al discloses a hair conditioning composition comprising quaternary ammonium compounds derived from dimethylaminopropyl amides (column 1, lines 56-64). See, column 1, lines 26-38, which states that quaternary ammonium compounds are used to enhance substantivity.

US Patent 4,923,642 to Rutzen et al discloses quaternary ammonium compounds produced by the reaction of epoxy fatty acid ethers with an alcohol (column 6, lines 24-46).

US Patent No. 4,940,785 to Stober et al discloses a method for preparing cellulose ethers containing quaternary nitrogen by reacting cellulose with QUAB (2,3-epoxypropyltrimethyl ammonium chloride) (column 4, lines 51-63), i.e. see formulas in Abstract and the top of column 2. These modified cellulose products are used in cosmetics (hair treatment), in textiles (softener, antistatic agents), in the paper industry, in flotation and flocculation and in drilling fluids.

US Patent No. 4,950,468 to Nakamura et al discloses a hair treating composition containing stearyltrimethyl ammonium chloride (column 2, lines 53-56).

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The following US Pat nts teach the use of panthenol in hair care products:

4,220,167 to Newell;

4,610,874 to Matravers;

4,897,262 to Nandagiri et al; and

4,725,433 to Matravers.

Newell at column 4, lines 13-16 discloses a "pantothenyl alcohol" in a hair composition.

'874 Matravers discloses the use of panthenol in a hair conditioner product.

Nandagiri et al at column 4, line 30 describes the use of panthenol in a non-aerosol hair-spray composition.

'433 Matravers discloses the use of panthenol in a hair care product. Further at column 2, lines 45-49, this patent discloses polymeric quaternary ammonium salt of hydroxyethylcellulose reacted with trimethyl/ammonium substituted epoxide (CTFA name: Polyquaternium 10) in a hair conditioner.

Manufacturing Chemist, July 1987, Alexander "Cationic Polymers for Skin & Hair Conditioning", describes polymers for skin and hair conditioning products as well as several techniques used to demonstrate the substantivity of these polymers on hair and skin, including the "Rubine dye tests".

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Alexander also describes the reaction of 2,3 epoxypentyl (trimethyl) ammonium chloride with one of the free hydroxy groups of guar gum to produce guar hydroxypentyl trimonium chloride having a charge density higher than other guar derivatives. The product commercially known as Jaguar C-13-S from Meyhall Chemical (Celanese), is said to confer conditioning properties to both hair and skin and can be used as a thickener for shampoos, liquid soaps, creme rinses, hand creams and lotions.

None of the aforecited references teach or suggest the quaternized panthenol compounds of this invention and their use in cosmetic product formulations.

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## OBJECTS AND SUMMARY OF THE INVENTION

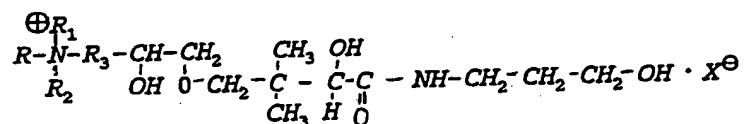
It is an object of this invention to provide a functional ingredient for use in cosmetic products, for example, hair styling products, hair care products, personal care products, sun care products, and skin care products.

It is a further object of this invention to provide a quaternized panthenol compound which provides enhanced substantivity to such cosmetic products.

It is a further object of this invention to provide a quaternized panthenol product which has unexpected compatibility with systems containing anionic surfactants, such as in shampoos, soaps, and emulsions.

It is still a further object of this invention to provide a method of enhancing the substantivity of panthenol.

All of the foregoing objects of this invention are achieved by a compound of the formula:



wherein, R, R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are each, independently, a straight or branched chain alkyl of 1-24 carbon atoms and X is a hal gen.

Preferably, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are alkyl of one carbon atom, R is a methyl (CH<sub>3</sub>) or a stearyl (C<sub>18</sub>H<sub>37</sub>) and X is chlorine.

The preferred compounds of this invention are the reaction product of d,l - panthenol and 2, 3 - epoxypropyl stearyl dimethyl ammonium chloride and the reaction product of d,l - panthenol and 2, 3 - epoxypropyl trimethyl ammonium chloride.

These compounds have enhanced substantivity when compared to panthenol and are preferably used in cosmetic products, such as hair styling products, hair care products, personal care products, sun care products, and skin care products.

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DETAILED DESCRIPTION OF THE INVENTION

5 Panthenol (Hoffman La Roche, Inc.; Tri-K Industries, Inc.; R.I.T.A. Corp.) is available in two forms, namely, the dextrorotatory isomer (d - panthenol) or the racemic form (d,l - panthenol). d - panthenol is a colorless, viscous liquid, while d,l-panthenol is a white, crystalline powder. d- and d,l-panthenol are both very soluble in water and alcohol, but are insoluble in fats and oils. Aqueous solutions of d- and d,l-panthenol are most stable in the pH range of 4 to 7, the optimum pH being approximately 6. Hydrolysis occurs at an increasing rate as the pH varies from the optimum pH.

10 Typical data on the properties of d- and d,l-panthenol are shown in Table I.

TABLE 1

Properties of d- and d,l-Panthenol

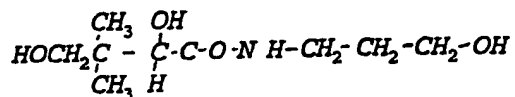
	d-Panthenol	d,l-Panthenol
Appearance	Viscous, clear liquid	Crystalline powder
5 Color	None	White
Solubility in Water (50%)	Clear, complete	Clear, complete
Color of Aqueous Solution	Colorless	Colorless
10 Solubility in Ethanol (50%)	Clear, complete	Clear, complete

15 Panthenol can be incorporated into cosmetic formulations without adjustments other than maintaining the pH conditions for the optimum stability of the compound. It may be incorporated directly into the aqueous phase of standard cosmetic preparations or, in the absence of an aqueous phase, intimately dispersed in the oil phase. Cosmetic formulations containing panthenol can be prepared in the usual manner with standard equipment. Likewise, the compounds of this invention can be incorporated in cosmetic formulations.

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Panthenol has the formula:



C<sub>9</sub>H<sub>19</sub> NO<sub>4</sub>, molecular weight 205.25.

Although it is preferred that the d - or d,l - panthenol compounds or mixtures thereof be utilized as a reactant, however by the use of the term "panthenol" herein it is contemplated that not only these compounds are contemplated but derivatives of panthenol are contemplated as well, for example, the ethers and thioethers of panthenol, see for example US Patent No. 3,230,228 to Erlemann, the entire disclosure of which is incorporated herein by reference.

The quaternized panthenol compounds of this invention can be derived from both the d-panthenol and d,l-panthenol, although it is preferred to utilize the d,l-panthenol.

The quaternized panthenol compounds of this invention are obtained by reacting a quaternary epoxide with panthenol in an alkaline medium in the presence of water.

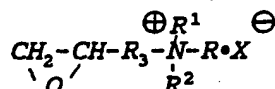
The reaction mixture is alkalized by the addition of 1 to 4% by weight of an alkaline metal or alkaline -

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earth metal hydroxide or oxid , or of an alkaline silicate and/or alkaline aluminate or of a mixture of alkaline hydroxid s or oxides r alkaline-earth hydroxides or oxides and alkaline carbonates or the mixture of one or more of these hydroxides, oxides, or carbonates with an alkaline silicate and/or alkaline aluminate.

It is preferred to use from 1 to 3% by weight of an alkaline hydroxide or from 3 to 4% by weight of the alkaline - earth hydroxide or oxide in relation to the amount of panthenol in each instance.

The quaternary epoxides or mixtures of epoxides used to react with the panthenol are of the general formula:



wherein R, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> correspond to the same or different alkyl groups, branched or straight chained, with 1 to 24 carbon atoms and X is a halogen, preferably chlorine. Preferably R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are methyl and R is methyl (CH<sub>3</sub>) or stearyl (C<sub>18</sub>H<sub>37</sub>).

Instead of the quaternary epoxides, the corresponding chlorohydrins can also be used for purposes of the invention in which instance the reaction to form

the epoxides corresponding to the above formulas, which react in turn with the panthenol or its derivatives, takes place at the latest in the reaction medium. However, in this instance, the stoichiometric amount of alkali for converting the chlorohydrins into the epoxides must be added in addition to a catalytic amount. Panthenol or its derivatives are then added to the reaction mixture.

A neutralization of the final product may be necessary, depending on the application. An inorganic acid, e.g. adipic acid, lactic acid, may be added during the mixing process or after reaction in order to obtain such a neutral product.

The range of the reaction temperature of the process extends from about 5°C to about 75°C, especially from about 40°C to 60° C.

The sequence of addition of the reagent to the panthenol in a reaction vessel is not critical.

Preferred commercially available chlorohydrins for producing epoxides for reacting with panthenol are:



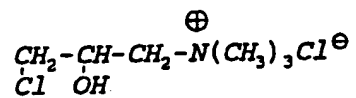
Q U A B 188 (D gussa Corp.)

Q U A T 188 (D w Chemical Corp.)

3-Chl ro-2 hydr xypropyl trimethylamm nium chl rid

Structural Formula:

5



Molecular formula:

 $\text{C}_6\text{H}_{15}\text{Cl}_2\text{NO}$ 

Molecular weight:

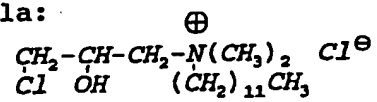
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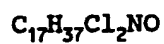
Q U A B 342 (Degussa Corp.)

3-Chloro-2-hydroxypropyl-dimethyldodecylammonium chloride

Structural formula:



Molecular formula:



Molecular weight:

342

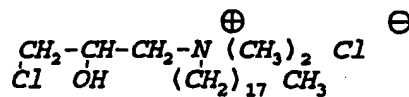
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Q U A B 426 (Degussa Corp.)

3-Chloro-2-hydroxypropyl-N.N.N-  
dimethyloctadecylammonium chloride

Structural Formula:



5      Molecular Formula:       $\text{C}_{23}\text{H}_{49}\text{Cl}_2\text{NO}$   
 Molecular Weight:      426

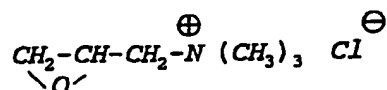
A preferred commercially available quaternary  
 epoxide is:

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Q U A B 151 (Degussa C rp.)

Glycidyltrimethylammonium chloride  
2, 3-Epoxypropyltrimethylammonium chloride

Structural Formula:

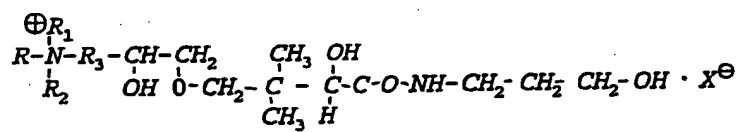


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Molecular Formula:  $\text{C}_6\text{H}_{14}\text{Cl NO}$ 

Molecular Weight: 151

Some commercially viable and preferred compounds of  
 this invention of the formula:



are:

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Panthenol	R	R1	R2	R3	X-	Name
d,l	CH3	CH3	CH3	CH3	Cl	trimethyl quaternized panthenol
d,l	C18H37	CH3	CH3	CH2	Cl	stearyl dimethyl quaternized panthenol
d,l	C12H25	CH3	CH3	CH2	Cl	lauryl dimethyl quaternized panthenol
d	CH3	CH3	CH3	CH3	Cl	trimethyl quaternized d-panthenol
d	C18H37	CH3	CH3	CH2	Cl	stearyl dimethyl quaternized d-panthenol
d	C12H25	CH3	CH3	CH2	Cl	lauryl Dimethyl quaternized d-panthenol

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The types of compositions or formulations in which the compounds of this invention may be used are:

**Hair Styling Products, including:**

- Aerosol and Non-Aerosol Mousse
- Aerosol and Non-Aerosol Hair Spray
- Hair Sculpting (styling) Lotion
- Hair Styling Gel
- Curl Refresher Lotion
- Curl Activators

**Hair Care Products, including;**

- Shampoos
- Conditioners
- Hair Color, e.g. temporary, semi-permanent and permanent
- Permanent Waves
- Hair Relaxers
- Hair Bleach

**Personal Care Products, including;**

- (a) Bath products, e.g. bubble bath, shower gel, liquid hand soap, facial cleanser, bath soap

- (b) Shaving products, e.g. shaving cream, after shave lotion (hydroalcoholic and emulsion based)

Suncare Products, e.g. creams, lotions; and  
Skin Care, e.g. creams, lotions, tonics.

The quaternized panthenol compounds of this invention essentially have all of the functional properties of panthenol, with the addition of providing enhanced substantivity to the cosmetic product when compared to panthenol, as well as having enhanced surface activity, enhanced antistatic properties and enhanced lubricity when compared to panthenol. Similar to panthenol, the compounds of this invention can enhance the performance of hair care products, for example, increase the moisture retention of hair, prevent damage to hair during blow drying, reduce the formation of split ends, condition without buildup, and impart sheen and lustre to the hair. Likewise, the compounds of this invention can be quickly absorbed into the skin and hair, and can be ideal for use in aftershaves, colognes, creams, lotions, and suntan products.

In addition to its moisturizing qualities, the compounds of this invention are substantially colorless,

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odorless, stainless and completely safe. They are freely soluble in water and alcohol and are stable in a critical mutual pH range, making them compatible with other ingredients. Unexpectedly, the compounds of this invention exhibit chemical compatibility with a broad range of anionic compounds commonly used in cosmetic formulations unlike most cationic conditioning agents which are typically incompatible with such anionics. (See, for example, Examples V and X).

It is anticipated that the compounds of this invention when used in hair and skin care products will permit provitamin B<sub>5</sub> (panthenol) to be converted to pantothenic acid (vitamin B<sub>5</sub>) in hair and skin. It is also anticipated that the product will penetrate deeply into the hair shaft, have long lasting moisture control, independent of the atmospheric conditions, prevent over drying of hair and scalp caused by blow dryers, reduce considerably the formation of split ends due to combing and brushing, reduce hair tangling by smoothing the cuticle, provide for clean conditioning without buildup, repair damage caused by chemical and mechanical treatment, e.g. perming, over-processing, combing, brushing and coloring, slow down the aging process (wear and tear of hair) caused by over-shampooing, brushing, and combing (cuticle damage, cortex weakening), increase

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the tensile strength of hair (especially beneficial to bleached hair), impart sheen and lustre.

Preferred levels of use of the quaternized panth nol of this invention are from about .1% to about 20% by weight in the skin care or hair product.

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EXAMPLE

In the following Examples, the qualitative test for measuring the substantivity of the compounds on hair was the Rubine Dye Test using Pyrazol Fast Bordeaux, as described in US Patent No. 3,769,398 to Hewitt and Crawford et al, J. Soc. Cosmet. Chem. 31, 273-278 (1980), the entire disclosures of which are incorporated herein by reference. The intensity of the residual pink color, after rinsing, on a hair swatch previously treated with the compound, is an indication of the degree of deposition of the compound onto the hair. Absence of pink color points to a lack of substantivity.

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**EXAMPLE I**  
**TRIMETHYL QUATERNIZED PANTHENOL**

In a one liter reaction flask, fitted with a stirrer, thermometer reflux condenser, heating mantle and a feed funnel, 205 grams of deionized water was charged. 205 grams (1 mole) of d,l-panthenol was charged in the water and stirred until dissolved. In a separate, stirred, one liter vessel, 376 grams (1 mole) of 50% aqueous QUAB 188 (3-Chloro-2-hydroxypropyl trimethylammonium chloride) was reacted with approximately 80 grams (1 mole) of 50% aqueous sodium hydroxide solution, to form a solution of QUAB 151 (2, 3-Epoxypropyl trimethyl ammonium chloride), to a pH of ~9.5. The batch was heated to 50°-60°C, and the QUAB 151 solution was added to the panthenol solution through the feed funnel. The pH of the reaction mixture was checked, and adjusted to ~9.5 with a small additional amount of 50% sodium hydroxide solution, as required. The batch was then agitated at 50°-60°C for a four hour period to assure complete reaction. The pH of the batch was then adjusted to 6.5-8.0 with a small amount of lactic acid. The resultant product was a clear yellow solution, containing approximately 50% of trimethyl quaternized panthenol. An in vitro efficacy test of this material versus a panthenol solution of comparable

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concentration, was tested for uptake on human hair swatches and showed an approximate 7% greater uptake than the unquaternized panthenol.

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EXAMPLE II**STEARYL DIMETHYL QUATERNIZED PANTHENOL**

In a two liter reaction flask, fitted with a stirrer, thermometer, reflux condenser, heating mantle and a feed funnel, 205 grams of deionized water was charged. 205 grams (1 mole) of d,l- panthenol was charged into the water and stirred until dissolved. In a separate stirred one liter vessel, 852 grams (1 mole) of 50% aqueous QUAB 426 (3-Chloro-2-hydroxypropyl stearyl dimethylammonium chloride) was reacted with approximately 80 grams (1 mole) of 50% aqueous sodium hydroxide solution, to form a solution of QUAB 393 (2,3-Epoxypropyl stearyl dimethyl ammonium chloride), to a pH of ~9.5. The batch was heated to 50°-60°C, and the QUAB 393 solution was added to the panthenol solution through the feed funnel. The pH of the reaction mixture was checked, and adjusted to ~9.5 with a small additional amount of 50% sodium hydroxide solution, as required. The batch was then agitated at 50°-60°C for a four hour period to assure complete reaction. The pH of the batch was then adjusted to 6.5-8.0 with a small amount of lactic acid. The resultant product was a clear yellow solution, containing approximately 50% solids, of which approximately 43% was stearyl dimethyl quaternized panthenol. An in vitro efficacy test of this material versus a 50% panthenol

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solution was tested for uptake on human hair swatches and showed an approximate 27% greater uptake than the unquaternized panthenol. Adjusting the results for concentration of active material, the stearyl dimethyl quaternized panthenol showed an approximate 31% greater uptake than the unquaternized panthenol.

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EXAMPLE III  
SUBSTANTIVITY

SAMPLE 1: Panthenol  
50% Aqueous solution.  
SAMPLE 2: Stearyl dimethyl quaternized panthenol,  
50% solids Aqueous solution (Example II)

Rubine Dye uptake as a measure of substantivity.

Four tresses of Demeo Natural White Hair weighing approximately 0.5 grams each were immersed in 15 grams of the appropriate solution (i.e. positive control, negative control and test samples) for a period of not less than 5 minutes. Each tress was then rinsed five times with 100 ml of water at 120°F.

The tresses were then immersed in a solution of fast Rubine dye for 15 minutes, rinsed five times with 100 ml of water at 105° F, then air dried overnight on filter paper. Each tress was weighed directly into a tared beaker. The dye was stripped from the hair and the solution then brought to the volume with deionized water. The transmission of each sample was then read at 520 nm and its absorbance adjusted to the weight of the hair sample. The dye concentration was calculated from a standard calibration curve.

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Panthenol demonstrated an uptake at a level of 52.35 mg of dye/50 gm of hair; representing a 36.91% uptake with respect to the positive control.

Stearyl dimethyl quaternized panthenol demonstrated an uptake at a level of 66.30 mg of dye/50 gm of hair; representing a 46.74% uptake with respect to the positive control.

Therefore, within the limits of detection imposed by this study, stearyl dimethyl quaternized panthenol (50% solids Aqueous solution), exhibited superior uptake capability by 31% when compared with Panthenol, (50% Aqueous solution), when adjusted for concentration of active material.

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FORMULATIONSEXAMPLE IVHair Sculpting L t i n

<u>C.T.F.A. Name</u>	<u>Ingredients/Trade Name</u>	<u>%w/w</u>	<u>Function</u>
Phase A			
Water	Deionized Water	86.9	Solvent
PVP/Dimethylaminomethacrylate Copolymer	Copolymer 845 <sup>1</sup>	5.0	Hair Fixative
Vinylcaprolactam/PVP/Dimethylaminoethylmethacrylate	Gaffix VC-713 <sup>1</sup>	2.0	Hair Fixative
INVENTION	Quaternized panthenol <sup>2</sup>	1.0	Hair Conditioner and Detangler Bodying Agent
Phase B			
SD Alcohol 40	SD Alcohol 40	5.0	Solvent
Fragrance	Fragrance E 6367 <sup>3</sup>	0.1	Fragrance
		100.00	

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<sup>1</sup>GAF Chemicals Corporation<sup>2</sup>Example II herein<sup>3</sup>Shaw Mudge and Company

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Procedure: The water was weighed into a beaker. Each Phase A ingredient was then added to the water phase in the order listed and mixed thoroughly after the addition of each ingredient. The fragrance was dissolved in the alcohol and Phase B was added to Phase A and mixed until clear and uniform.

Properties of Completed Formula:

The product was a clear, pourable liquid styling lotion. The quaternized panthenol was compatible with the hair fixative polymer. The formulation provided excellent wet and dry combing body to the hair and appeared to improve hair curl.

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EXAMPLE VConditioning Shampoo

<u>Phase</u>	<u>CIFA Name</u>	<u>Ingredients</u>	<u>%w/w</u>	<u>Function</u>
A	Water	Deionized Water	56.95	Solvent
B	Sodium Lauryl Ether Sulfate	Standapol ES-2 <sup>1</sup>	30.00	Cleanser
C	Cetyl Betaine	Tritaine PB <sup>2</sup>	7.00	Cleanser
	Same	Methylparaben <sup>2</sup>	0.15	Preservative
	Same	Propylparaben <sup>2</sup>	0.05	Preservative
	Tetrasodium EDTA	Kelate 220 <sup>2</sup>	0.05	Chelating Agent
D	Cocamide DEA	Standamid KD <sup>1</sup>	3.00	Foam Booster
E	Imidazolidinyl Urea	Tristat IU <sup>2</sup>	0.30	Preservative
	Same	Deionized Water	1.00	Solvent
F	Fragrance	Fragrance E6367 <sup>3</sup>	0.10	Fragrance
G	Same	Citric Acid (50% aq. soln.)	0.40	pH Adjuster

<sup>1</sup>Henkel Corporation, COSPHA/CD<sup>2</sup>Tri-K Industries, Inc.<sup>3</sup>Shaw Mudge and Company

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H INVENTION

quaternized panthenol<sup>4</sup> 1.00

Hair  
Conditioner,  
Hair Bodying  
Agent

100.00

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<sup>4</sup>Example II herein

SUBSTITUTE SHEET

Procedure: Phase A was heated to 55°C. Phase B was added and mixed until uniform. Phase C ingredients were added in the order listed and mixed until uniform. When the batch cooled to 45°C, Phase E and Phase F were added and the batch was mixed until uniform. The pH was adjusted with Citric Acid. Phase H was added and the batch was mixed until uniform.

Properties of Complete Formula:

The finished conditioning shampoo was a clear, medium viscosity liquid. The quaternized panthenol (although cationic) was compatible with the anionic surfactants that make up the shampoo. The formulation provided improved wet and dry combing, increased body to the hair and better hair curl.

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EXAMPLE VILeave-On Hair Conditioner

<u>Phase</u>	<u>C.T.F.A. Name</u>	<u>Ingredient/Trade Name</u>	<u>%w/w</u>	<u>Function</u>
A	Water	Deionized Water	40.00	Solvent
	Amodimethicone	Siltech E-2145C <sup>1</sup>	2.00	Wet
	(and) Tallowtri-			c o m b i n g ;
	monium Chloride			hair
	(and) Monoxynol-10			conditioner
B	Water	Deionized Water	50.80	Solvent
	PVP/Dimethylamino-	Pecogel GC-310 <sup>2</sup>	1.50	Hair
	ethylmethacrylate			Fixative
	Polycarbonyl			
	Polyglycol Ester			
	INVENTION	Quaternized panthenol <sup>3</sup>	2.00	Hair Condi-
				tioning and
				Hair Bodying
				Agent
C	Same	Propylene Glycol	1.25	Solvent
	Methylparaben	Trisept M <sup>1</sup>	0.15	Preservative

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<sup>1</sup>Tri-K Industries, Inc.<sup>2</sup>Phoenix Chemical, Inc.<sup>3</sup>Example II herein

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D	Imidazolidinyl Urea	Trisat IU <sup>1</sup>	0.30	Preservative
	Water	Deionized Water	<u>2.00</u>	Solvent
			100.00	

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Procedure: The Siltech E-2145CG emulsion was predispersed in the Phase A water in a beaker. The Phase "B" ingredients were dissolved one at a time into the remainder of the water and mixed until clear. Phase "C" ingredients were mixed until clear and uniform. Phase "A" was added to Phase "B" with agitation. Then Phase "C" and "D" were added and the batch was mixed until uniform. The resultant product had an off-white, translucent appearance and was able to be sprayed using a Calmar Mark II High Viscosity Head Yellow orifice spray dispenser.

Properties of Completed Formula:

The finished conditioner was a translucent, off-white liquid that can be applied by spraying through a non-aerosol pump dispenser. The product was left on the hair and did not rinse out. The quaternized panthenol was compatible with the cationic silicone emulsion (Siltech E-2145CG) and with the hair fixative polymer. The formulation provided good conditioning and hair bodying.

**SUBSTITUTE SHEET**



EXAMPLE VIIN n-Aeros 1 Hair Spray

<u>Phase</u>	<u>C.I.F.A. Name</u>	<u>Ingredients/Trade Name</u>	<u>%w/w</u>	<u>Function</u>
A	SD Alcohol 40 Vinylcaprolactam/ PVP/Dimethylamino- ethylmethacrylate Copolymer	SD Alcohol 40	91.35	Solvent
		Gaffix VC-713 <sup>1</sup>	8.00	Hair Fixative
B	INVENTION	Quaternized panthenol <sup>2</sup>	0.50	Hair Conditioner
C	Fragrance	Natural Citrus Bouquet	0.15	Fragrance
		#901219 <sup>3</sup>		
			100.00	

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<sup>1</sup>GAF Chemicals Corporation<sup>2</sup>Example II herein<sup>3</sup>FlavorScents, Inc.

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Procedure: Phase A was weighed into a beaker and was then mixed until clear and uniform. Phase B and then Phase C were added to Phase A while mixing. The batch was mixed until clear and uniform.

Properties of Complete Formula:

The finished hair spray was a clear, pourable liquid that can be sprayed on via a non-aerosol pump dispenser. The quaternized panthenol was compatible with the hair fixative polymer and with the ethanol. The formulation provided conditioning and plasticized the hair fixative polymer.

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**EXAMPLE VIII**  
**INTENSIVE HAIR CONDITIONER**

<u>Phase</u>	<u>C.I.F.A. Name</u>	<u>Ingredient/Trade Name</u>	<u>%w/w</u>	<u>Function</u>
A	Water	Deionized Water	67.35	Solvent
	Polyquarternium-10	Ucare Polymer JR 30M <sup>1</sup>	0.50	Conditioner
	Methylparaben	Trisept M <sup>2</sup>	0.15	Thickener Preservative
B	Stearylalkonium Chloride	Maquat SC-18 (25%) <sup>3</sup>	4.00	Antistat
	Cetrimonium Chloride	Ammonyx Cetac <sup>4</sup>	4.00	Detangler
	INVENTION	Quaternized panthenol <sup>5</sup>	4.00	Conditioner
C	Propylparaben	Trisept P <sup>2</sup>	0.10	Preservative
	Behenamidroparyl-dimethylamine	Catamol 2208 <sup>6</sup>	2.00	Emulsifier
	Behenate Emulsifying Wax NF	T-Wax <sup>2</sup>	8.00	Emulsifier

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<sup>1</sup>Amerchol Corporation

<sup>2</sup>Tri-K Industries, Inc.

<sup>3</sup>Mason Chemical Company

<sup>4</sup>Stepan Company

<sup>5</sup>Example II herein

<sup>6</sup>Phoenix Chemical, Inc.

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	Cetearyl Alcohol	Cetearyl Alcohol	3.00	Thickener
	Avocado Oil	Avocado Oil <sup>2</sup>	4.00	Emollient
	Tocopherol	Mixed Tocopherols EM-80 <sup>2</sup>	0.20	Antioxidant, Vitamin
D	Fragrance	Herbal Tea E-8387 <sup>7</sup>	0.20	Fragrance
E	Imidazolidinyl Urea	Tristat IU <sup>2</sup>	0.50	Preservative
	Water	Deionized Water	<u>2.00</u>	Solvent
			100.00	

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<sup>7</sup> Shaw Hudge and Company

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Procedure: Ucare Polymer JR was dispersed in the water. After the polymer was dispersed, the Methylparaben was added. Phase A was then heated to 60°C. Phase B was then added to Phase A while mixing. Phase C was heated to 70°C and then added to Phase AB while mixing with a side sweep agitator. The batch was cooled and mixed to 45°C and Phase D was added followed by Phase E. The batch was mixed and cooled to 40°C and poured into jars.

Properties of Complete Formula:

The finished conditioner was a thick, white cream. the formulation was meant to be applied to the hair, left on 5-20 minutes and then rinsed out. The quaternized panthenol was compatible with the other cationic ingredients in the formula. The formulation provided good conditioning and hair bodying especially on damaged, chemically processed (bleached and permed) hair.

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EXAMPLE IXHand and Body Lotion

<u>Phase</u>	<u>C.T.F.A. Name</u>	<u>Ingredients/Trade Name</u>	<u>%w/w</u>	<u>Function</u>
A	Water	Distilled Water	75.35	Solvent
B	Same	Glycerin	5.00	Humectant
	Methylparaben	Trisept M	0.20	Preservative
	Propylparaben	Trisept P	0.10	Preservative
C		Amigel <sup>1</sup>	0.40	Thickener
D	INVENTION	Quaternized panthenol <sup>2</sup>	2.00	Skin Conditioner
E	Emulsifying Wax N.F.	T-Wax <sup>1</sup>	3.50	Emulsifier
	Mineral Oil			
	(and) PEG-30			
	Lanolin (and)			
	Cetyl Alcohol	T Base <sup>1</sup>	2.00	Emulsifier
	Same	Avocado Oil <sup>1</sup>	2.50	Emollient
	Same	Jojoba Oil <sup>1</sup>	2.50	Emollient
	Squalane	Trilane <sup>1</sup>	5.00	Emollient
	Dimethicone	Siltech F-350 <sup>1</sup>	0.30	Emollient
	Tocopheryl Acetate	Vitamin E Acetate <sup>1</sup>	0.20	Vitamin

<sup>1</sup>Tri-K Industries, Inc.<sup>2</sup>Example II herein

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F Same  
Fragrance

Phenoxyethanol<sup>1</sup>  
Fragrance TC-316<sup>3</sup>

0.70  
0.25  
100.00

Preservative  
Fragrance

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<sup>3</sup>Shaw Mudge and Company

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Procedure: Phase A was heated to 75°C. The parabens were dispersed in the glycerin. The amigel was then dispersed into the glycerin. The glycerin mixture was added to the water and mixed vigorously with a propeller. Phase D was then added to water phase. Phase E was heated to 75°C and added to the water phase with mixing. Mixing was switched to side sweep agitation and the batch was cooled to 45°C. Phase F was then added to the batch. The batch was mixed and cooled to room temperature.

Properties of Completed Formula:

The finished lotion was a white, medium viscosity lotion. The quaternized panthenol was compatible with all of the nonionic ingredients in the formula. The formulation provided skin softening, smoothing and conditioning properties.

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EXAMPLE XNEUTROGENA<sup>TM</sup> SOAP BAR

<u>Phase</u>	<u>Ingredients/Trade Name</u>	<u>%w/w</u>	<u>Function</u>
A	Neutrogena <sup>TM</sup> Soap Bar <sup>1</sup>	98.0	Soap Bar
B	Quaternized panthenol <sup>2</sup>	2.0	Skin Conditioner

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<sup>1</sup>Neutrogena Corporation

<sup>2</sup>Example II herein

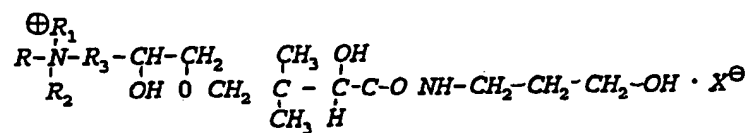
SUBSTITUTE SHEET

Phase A was warmed to 72°C, Phase B was added to Phase A with low shear mixing. The batch was cooled slightly and poured into molds. The finished soap bar was a clear, amber solid. The quaternized panthenol was compatible with the anionic soaps and surfactants in the Neutrogena™ soap bar. Use of quaternized panthenol in the bar improved the lather and provided perceivable skin conditioning benefits as evidenced by the improved after feel of the skin.

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AS CLAIMED IN THE CLAIMS

1. A compound of the formula:



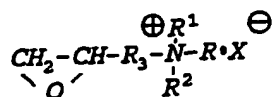
wherein R, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each independently, straight or branched chain alkyl of 1 to 24 carbon atoms

2. The compound of Claim 1, wherein  $R_1$ ,  $R_2$ , and  $R_3$  are methyl.
3. The compound of Claim 2 wherein R is stearyl ( $C_{18}H_{37}$ ).
4. The compound of Claim 2, wherein R is lauryl ( $C_{12}H_{25}$ ).
5. The compound of Claim 1, derived from d-panthenol.
6. The compound of Claim 2 wherein R is methyl.
7. The compound trimethyl quaternized panthenol.

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8. The compound stearyl dimethyl quaternized panthenol.

9. A compound which is the reaction product of d,l panthenol and



wherein R, R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are each independently straight or branched chain alkyl of 1 to 24 carbon atoms.

10. The compound of Claim 9, where R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are methyl.

11. The compound of Claim 10, wherein R is stearyl  
(C<sub>18</sub>H<sub>37</sub>).

12. The compound of Claim 10, wherein R is methyl.

13. The compound of Claim 10 where in R is lauryl ( $C_{12}H_{25}$ ).

14. A hair styling product comprising the compound of Claim 1.

15. An aerosol mousse comprising the compound of Claim 1.

16. A non-aerosol mousse comprising the compound of Claim 1.

17. An aerosol hair spray comprising the compound of Claim 1.

18. A non-aerosol hair spray comprising the compound of Claim 1.

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19. A hair sculpting lotion comprising the compound of Claim 1.

20. A hair styling gel comprising the compound of Claim 1.

21. A curl refresher lotion comprising the compound of Claim 1.

22. A curl activator comprising the compound of Claim 1.

23. A hair care product comprising the compound of Claim 1.

24. A shampoo product comprising the compound of Claim 1.

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25. A conditioner product comprising the compound of Claim 1.

26. A hair color product comprising the compound of Claim 1.

27. A permanent wave product comprising the compound of Claim 1.

28. A hair relaxer product comprising the compound of Claim 1.

29. A hair bleach product comprising the compound of Claim 1.

30. A personal care product comprising the compound of Claim 1.

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31. A bath product comprising the compound of Claim 1.

32. A shaving product comprising the compound of Claim 1.

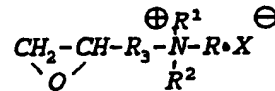
33. A sun care product comprising the compound of Claim 1.

34. A skin care product comprising the compound of Claim 1.

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35. A method of enhancing the substantivity of panthenol comprising reacting panthenol with a compound of the formula



wherein R, R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are each independently straight or branched chain alkyl of 1 to 24 carbon atoms.

36. The method of Claim 35, wherein  $R_1$ ,  $R_2$ , and  $R_3$  are methyl.

37. The method of Claim 36, wherein R is stearyl ( $C_{18}H_{37}$ ).

38. The method of Claim 36, wherein R is methyl.

39. The method of Claim 36 wherein R is lauryl (C<sub>12</sub>H<sub>25</sub>).

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40. The method of Claim 35 wherein panthenol is d-panthenol.

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# INTERNATIONAL SEARCH REPORT

PCT/US92/00985

International Application No.

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(5) C07C 237/08		
US CL. 564/197; 424/47,59,70,71,73		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
US	564/197,203; 424/47,59,70,71,73	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
Chemical Abstracts Service (1967-1992), U.S. Automated Patent System (1975-1992) Terms: Panthenol, ammonium; strucutre		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b>		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages *	Relevant to Claim No. **
Y	US, A, 4,940,785 (STOBER ET AL), 10 July 1990 column 2, line 57, to column 3, line 50	35-40
A	US, A, 3,230,228 (ERLEMANN, ET AL); 18 January 1966 column 1, lines 23-49	1-34
A	US, A, 3,766,267 (ZAK et al), 16 October 1973, column 2, lines 34-63	1-34
A	US, A, 3,396,045 (ERLEMANN, et al), 13 Febraury 1968, column 1, lines 22-29	
<p>* Special categories of cited documents: *</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
22 April 1992	15 MAY 1992	
International Searching Authority	Signature of Authorizing Officer	
ISA/US	Carolyn S. Elmore	